First principles modeling of Segregation of Nd to YAG grain boundarie

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14. ABSTRACT

Calculations show that Nd doping in bulk is endothermic and it agrees with experiments which show that only a very small amount can be added in bulk. However, there is a large segregation energy on surface and Nd doping is energetically favorable. An interesting finding is that Al replacement by Nd at the surface is highly exothermic. We expect similar trends on grain boundaries though segregation energies will be lower.

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University of Tokyo.

Objectives

(1) study bulk yttrium aluminum garnate (YAG) and compare the calculated bulk atomic structure with the experimetal data
(2) extend calculations to study the effects of substitutional dopings on a rare earth (Nd) doped system, using a supercell with Nd atom placed in the center
(3) perform structure calculations using a supercell with sigma 3 grain boundary and Nd atom placed on the grain boundary
(4) perforn the structure calculations as noted in item 3 with sigma 9 grain boundary, and
(5) perform analysis/interpretation and write report.

Method of Calculations

We have used ab initio density functional based projected augmented wave (PAW) method within the pseudopotential approach and the generalized gradient approximation for the exchange-correlation energy. A plane wave basis set is used for the wavefunctions. The calculations of doped and defect systems have been done using a supercell method. The energies of the pure and doped YAG systems have been calculated to obtain segregation tendencies. Nd atom is treated as trivalent and the calculations have been done without spin-polarization. Both Y and Al sites have been considered for substitution by Nd atom. The concentration of Nd is in the range of 0.5 – 0.6 at. %.

Results

1. Calculation of Bulk YAG structure

Total energy calculations have been performed on YAG ($Y_3Al_5O_{12}$) by considering 160 atoms in the unit cell. For such large unit cells only the gamma point has been used for k-space integration. The initial structure is taken from experimental results, but it is fully optimized. The resulting lattice constant, a, is

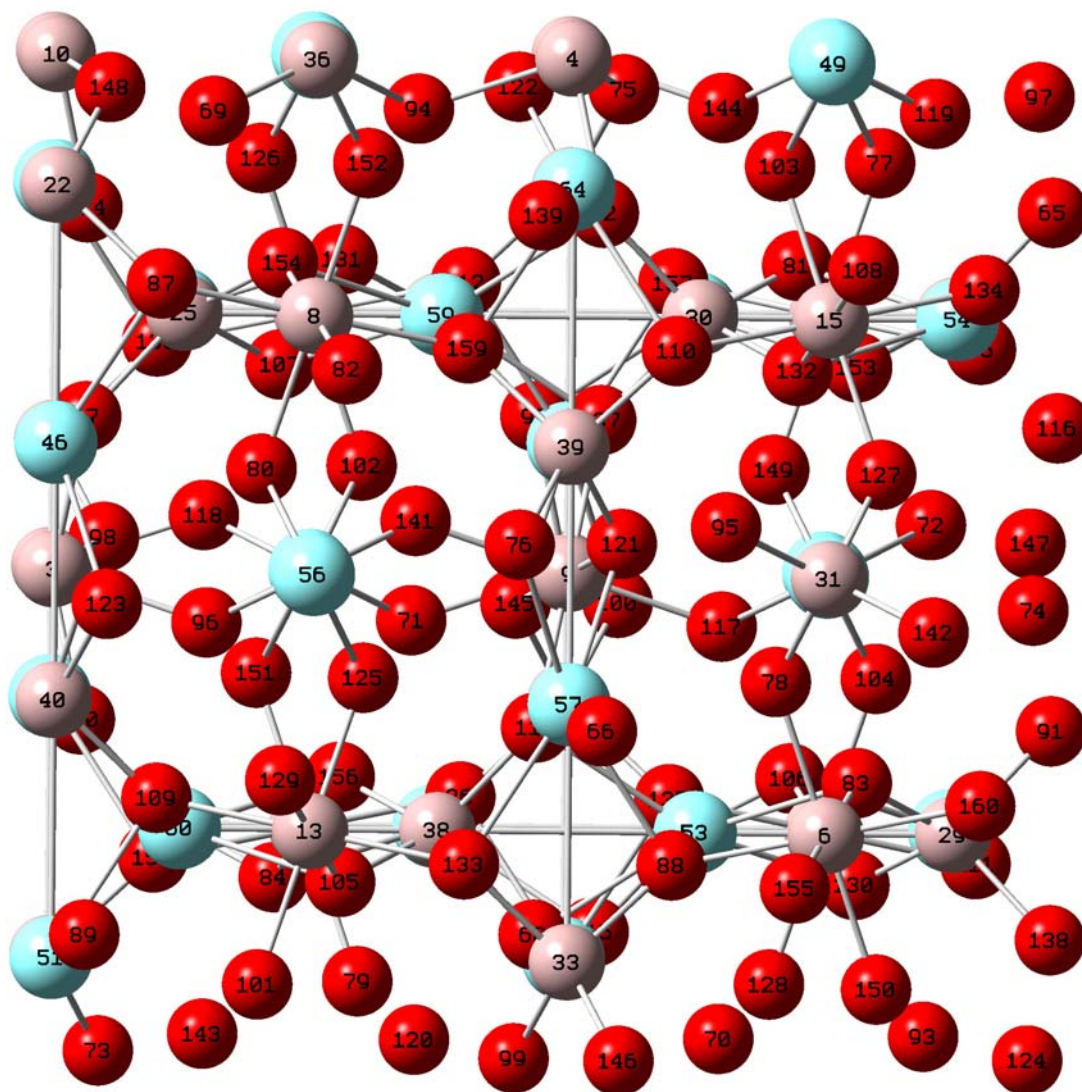Calculated   a = 12.125
  Experimental a =   12.000
Error   ~ 1%

Therefore the agreement with the experiment data is excellent.

The figure shows variation of energy as a function of lattice constant a.

Variation of E with a

YAG
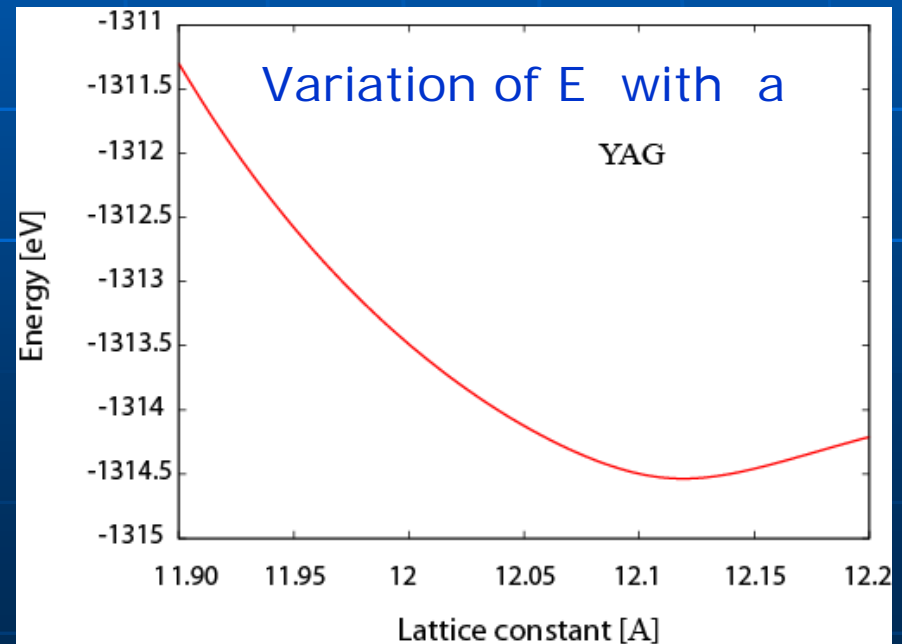
Unit cell of bulk YAG

Red   O
Violet Al
Blue   Y

2. Nd doped in bulk at a Y site

One Y atom was replaced by Nd around the center of the unit cell. The lattice constant of the unit cell was kept the same as for pure YAG, but the positions of atoms were fully relaxed. The concentration of Nd is 1 in 160 atoms. The optimized structure is shown below:

Substitution of Nd is endothermic by 0.42 eV/Nd atom. This energy cost may be reduced slightly if the unit cell is also optimized.
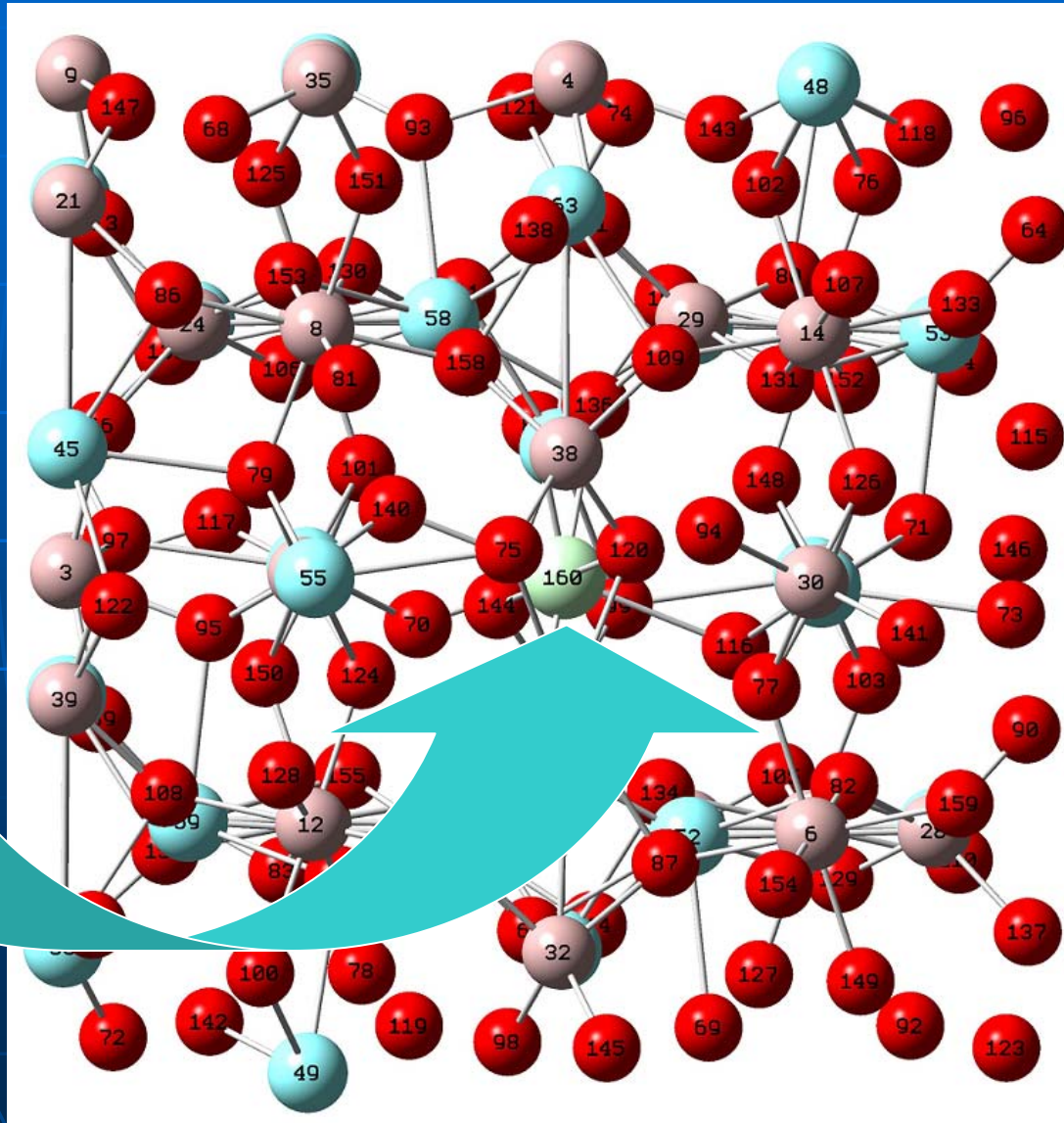
This calculation therefore shows that Nd doping is generally unfavorable in bulk.

Behind 31 Is Nd
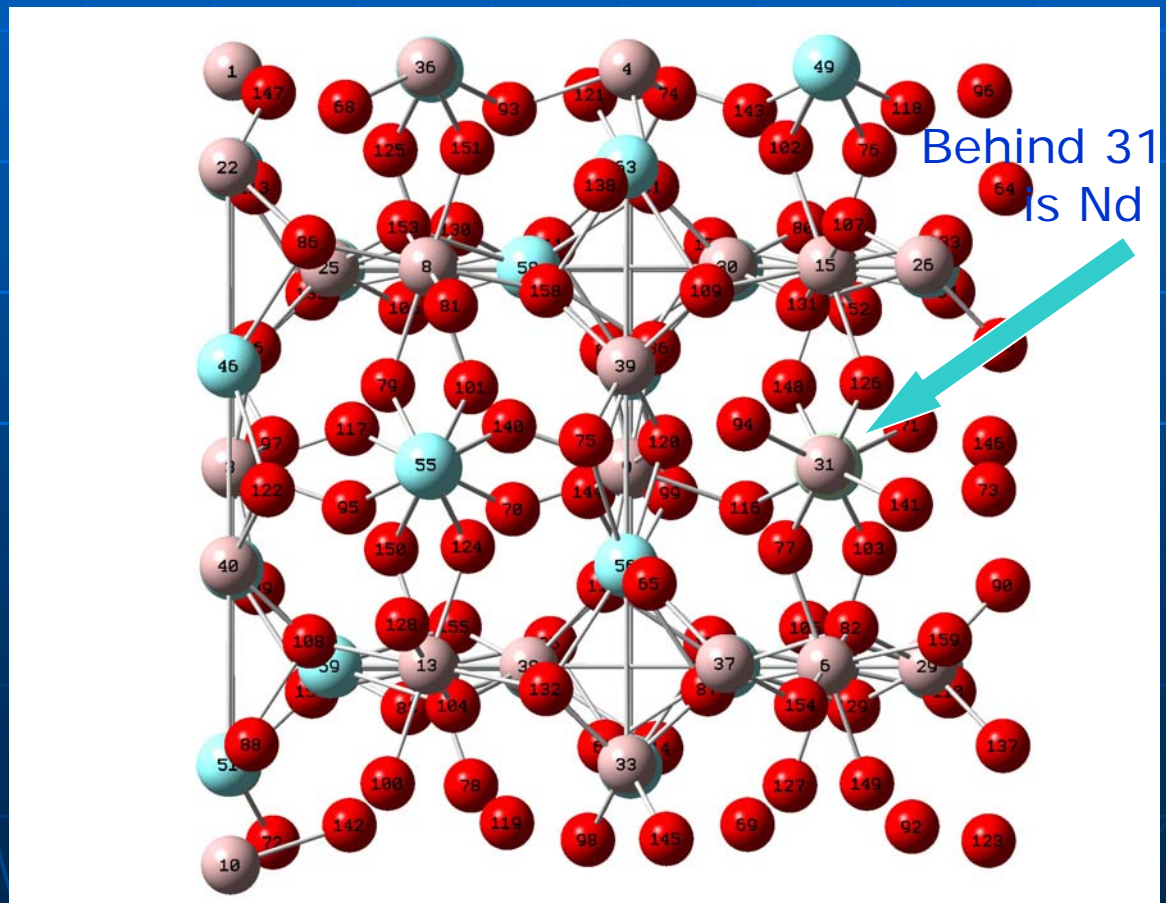
Nd doping on an octahedral Al site

Atom 160 at the center of O octahedron is Nd

Nd at octahedral Al site costs 0.23 eV. Again this energy will reduce slightly if lattice constant is optimized.

Such sites seem to be better for Nd doping.

3. Surfaces/interfaces

As the calculations for grain boundaries are very demanding, we decided to first study a surface of YAG to obtain some insight as often segregation behavior on surfaces and interfaces has similar tendencies. It turned out that even treating a surface is complex as in the first place it is not clear how to cut a surface. Of course in an experiment it can be easily done but the question will be what is the structure and how a surface terminates. This will have direct consequence for grain boundaries. We considered (001) surface and found that there is no unique way to prepare a surface which maintains stoichiometry. Therefore we tried a few configurations with a slab geometry and in the next figure we have shown a low energy (001) surface with bulk stoichiometry. It was difficult to obtain self-consistency as charge flow from some sites was necessary. This also leads to significant distortion in the structure. In order to avoid charge transfers from one place to another, we also considered a supercell with $Al_{52}Y_{32}O_{120}$ composition. The optimized structure is also shown for comparison. In this case the distortion in structure is less. We further substituted Nd on a Y or Al site to find out which site is more preferred.

Continued ....

Also using the same slab we calculated the energy of Nd substitution inside the slab which should be close to the energy of substitution of Nd in bulk. As the calculation conditions for bulk and the surface are the same, this will give the right tendencies for Nd segregation. Also in these calculations the relaxation of the lattice in z-direction is taken into account, though in the x and y directions, the lattice constant is taken to be the same as in bulk. There are different Al and Y sites in bulk and at surfaces and we tried to calculate the behavior for a few cases in order to find energy differences.

Slab for (001) surface calculations
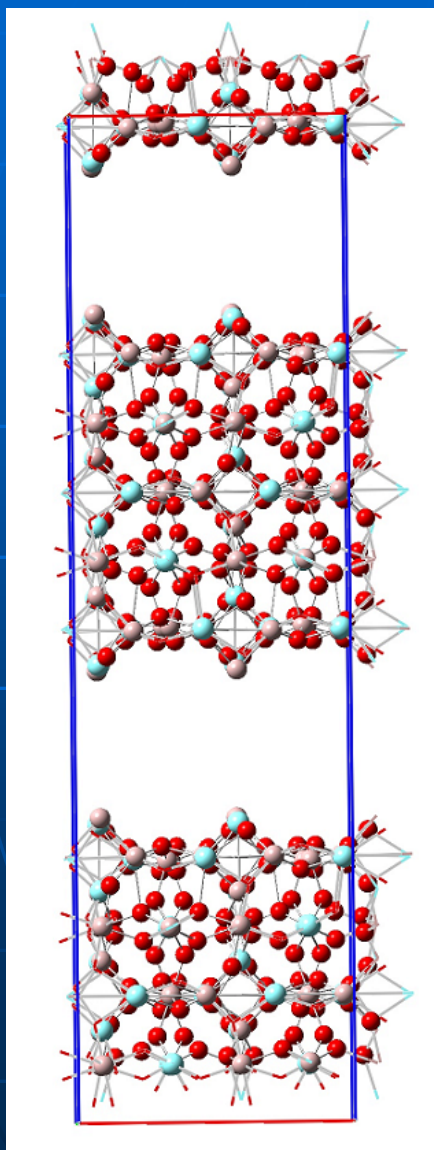
Al52Y32O120

The figure shows two unit cells along the z-direction. It is repeated along the x and y directions. The compositions are taken to be Al50Y30O120 and Al52Y32O120. The latter composition has excess of Al and Y atoms. This was prepared in order to have symmetric unit cell.
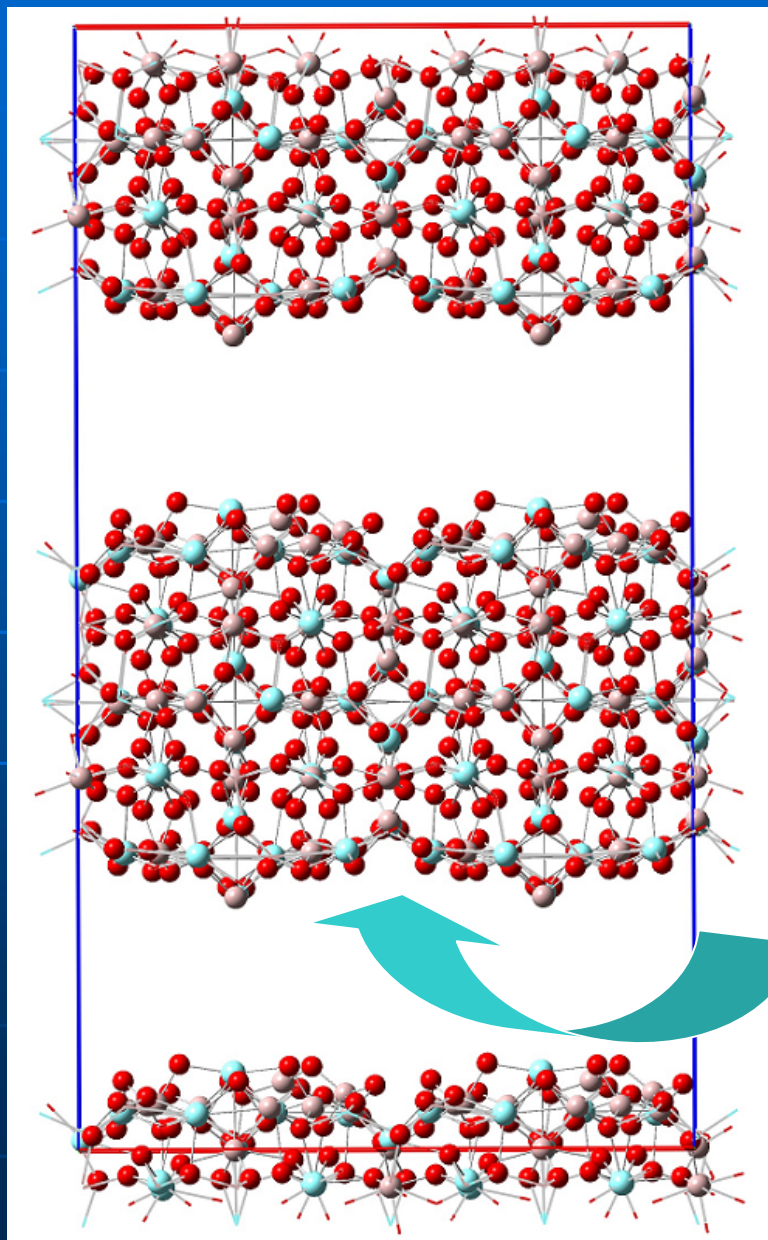

One Y atom replaced with surface Nd
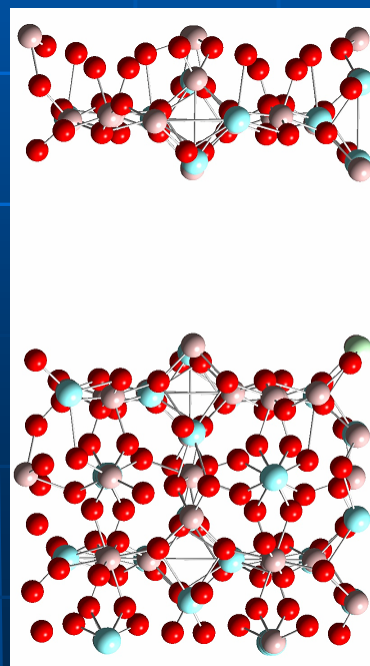
Energy gain in Substituting Y by Nd on surface is 0.14 eV.

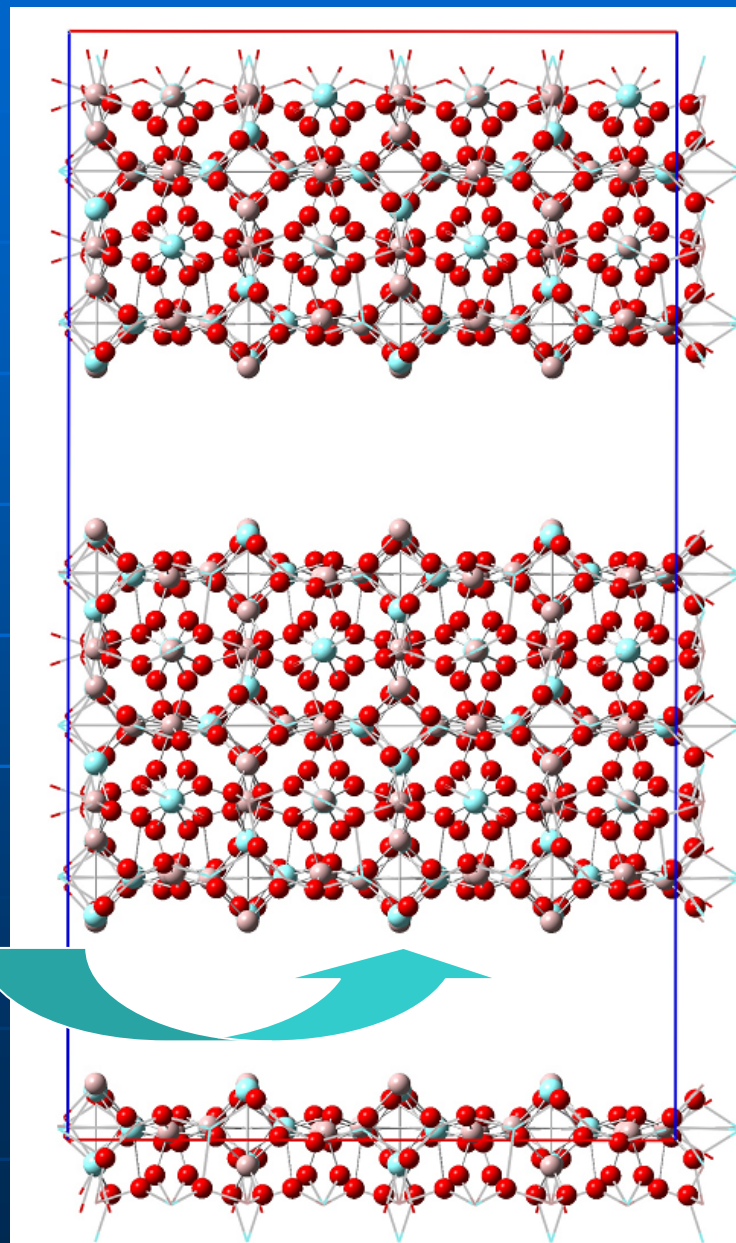Energy cost to replace Y by Nd inside the slab is 0.43 eV which is very close to the value 0.42 eV for bulk cal.

Al50Y30O120   Al52Y32O120   (Undoped)

surface

surface

2 unit cells along x and z directions

Al50Y29NdO120

Al52Y31NdO120 (Doped)

Nd
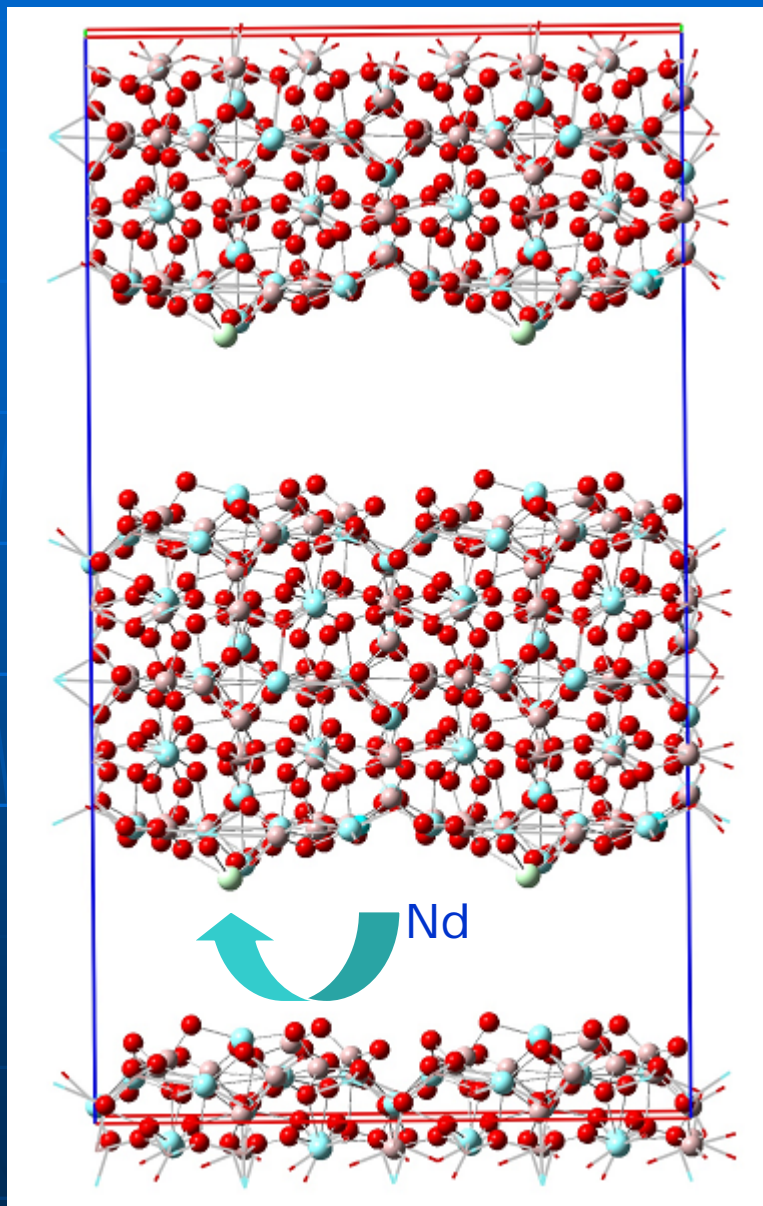
Nd
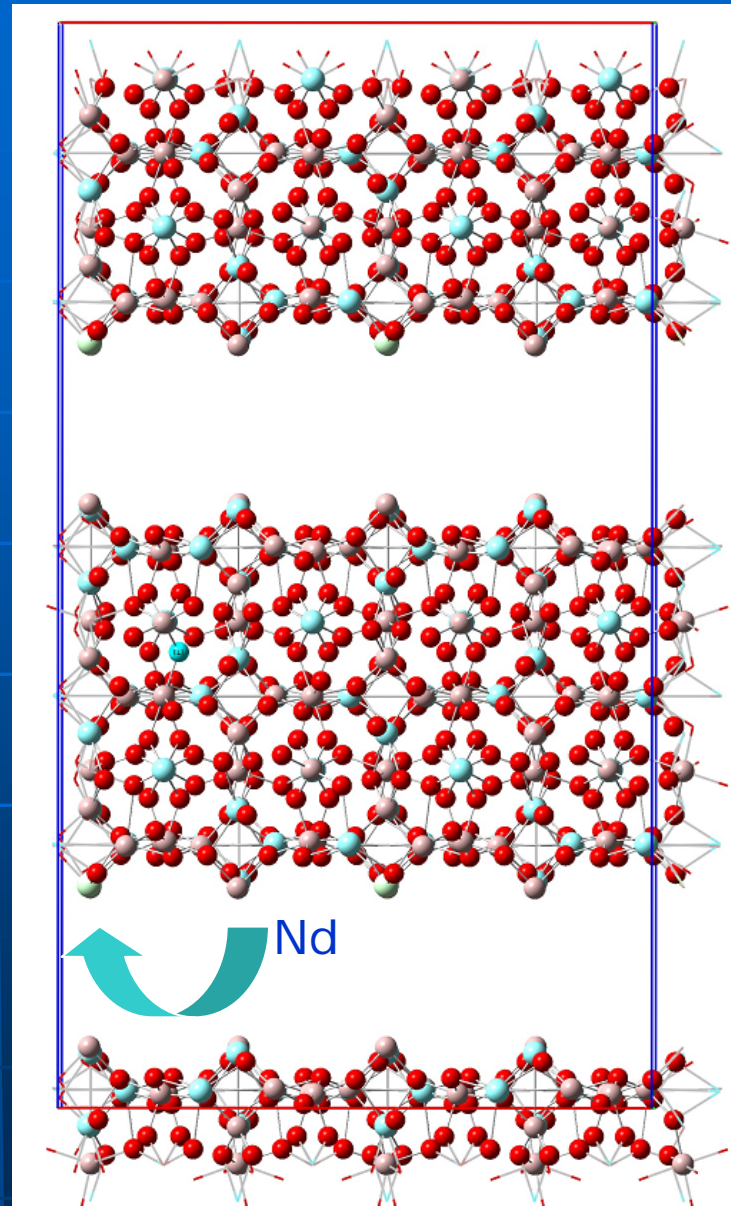
Segregation energy

Considering the Al52Y32O120 surface, the segregation energy when a Nd atom segregates from bulk to a surface Y site is 0.57 eV. This is a large energy and therefore Nd has strong tendency to segregate at surface. I expect a similar trend for grain boundaries though the segregation energy would be reduced.

Further calculations where Nd replaces an Al atom show that the energy gain is even much higher as compared to Y site. We find that if an Nd atom is substituted on a bulk octahedral Al site, then the energy cost is o.23 eV which is lower as compared to the Y site. Therefore we conclude that in bulk Nd doping is endothermic on both Y and Al sites. However on the surface there is a large gain of 0.96 eV in energy when an Al atom is replaced by Nd, Which is much higher as compared to substitution on Y site. Therefore on surface Nd would preferably occupy Al sites. These results show that there is a large gain in energy by doping Nd on a surface. We expect a similar tendency on grain boundaries though the energy gains will be lower. These results agree with the experiments which show that much higher concentrations of Nd can be doped in ceramic YAG material.

Continued ....

For the stoichiometric surface Al50Y30O120, the segregation energy is much higher (3.63 eV). This result should be taken with care as it will depend which sites have been taken in bulk and surface for Doping.

Conclusions

Our calculations show that Nd doping in bulk is endothermic and it agrees with experiments which show that only a very small amount Can be added in bulk. However, there is a large segregation energy on Surface and Nd doping is energetically favorable. An interesting finding Is that Al replacement by Nd at the surface is highly exothermic. We Expect similar trends on grain boundaries though segregation energies will be lower.

Further studies

We will continue to explore all the different Al and Y sites and also doping by two Nd atoms which could tell us if clustering of Nd atoms is favored. We shall continue to explore more on the surface structure and study $\Sigma3$ grain boundary which will be very heavy calculation. I feel that a full ab initio calculation on $\Sigma9$ grain boundary may not be doable as it would involve about 1500 atoms. However, the obtained results would be a good guide to use approximate methods such as those implemented in GULP program and understand more on the doping in grain boundary. Lastly, we have treated Nd as trivalent and ignored f electrons. This is a good approximation as f electrons will not contribute very significantly to bonding. We did some calculations including f electrons also and with magnetic solutions. These results are not sufficient to merit a discussion here. However, I intend to continue some effort in this direction to explore fully the properties of YAG material. To my knowledge there are only a couple of papers on bulk from ab initio methods and this study goes much beyond those studies and include surface effects. We have learnt significantly about this material and the information obtained would be very helpful to develop understanding of defects and grain boundaries and the related phenomena in YAG.